A QUANTUM MECHANICAL MODEL FOR USE BY SEAC IN THE CALCULATION OF CHEMICAL TRANSITION PROBABILITIES

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HYDROCARBON RESEARCH, INC.

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A Summary Report

Introduction

The work at Hydrocarbon Research, Inc. under Contract N-ONR-737 with the Office of Naval Research has been devoted to the development of transition probabilities for displacement reactions in a form suitable for calculation on large scale automatic computing machinery. The formulation of the transition probabilities is based upon the quantum theory of chemical kinetics developed previously by the authors[1]. The present work is part of a combined experimental and theoretical study of hydrogen-oxygen flames carried out jointly by Hydrocarbon Research, Inc. and the National Bureau of Standards, and the calculations based upon the model described here are to be carried out on SEAC, the automatic computer of the Bureau of Standards. Final coding of the problem for SEAC is currently being performed at the Computation Laboratory of the Bureau.

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(1) S. Golden and A. M. Peiser, "The Quantum Mechanics of Chemical Kinetics of Homogeneous Gas Phase Reactions", J. Chem. Phys. (17) 1949, pp. 630-643. The model used here differs from the earlier one in several important ways, in particular with regard to the treatment of the scattering and the chemical potentials.

The immediate objective has been to provide a means of calculating transition probabilities for the reactions

$$O_2 + H \longrightarrow OH + O$$

$$H_2 + O \longrightarrow OH + H,$$

but the formulation is sufficiently general so that it may be applied to a large class of displacement reactions.

The principal aim of the present work has been to arrive at a method of computation that (1) would not require machine capacity in excess of that of SEAC, and (2) could be carried out on SEAC in minimal time. We have succeeded in satisfying the first of these requirements. Precise statements concerning computing time cannot be made until the coding is completed, but the representatives of the Computation Laboratory have estimated that a single transition (from a given vibration-rotation state of the reactants to a given vibration-rotation state of the products) can be computed in under five minutes. On this basis, it appears that 40 - 50 hours of computing time will be required to calculate a given reaction at a given temperature.

The Mathematical Model

The formula for computing a given transition probability, which has been arrived at as the result of previous studies, may

T = temperature, ^{o}K.

n, m = quantum numbers corresponding to vibration for initial and final molecules, respectively;

K, L = quantum numbers corresponding to rotation for initial and final molecules, respectively;

$h_n(x)$ = normalized Hermite polynomial of order n;

$j_\lambda(x)$ = spherical Bessel function of order λ,

$$j_\lambda(x) = \sqrt{\frac{\pi}{2x}}\ J_\lambda(x)$$

$P_s(u)$ = Legendre polynomial of order s;

E_1, E_2 = discrete energy levels for initial and final molecule, respectively ;

$$\gamma = \frac{1}{kT}(E_2 - E_1) \ ;$$

$$\lambda_k = \sqrt{K_1 + k(k+1)} \ ;$$

$$\mu_l = \sqrt{K_2 + l(l+1)} \ .$$

The quantities θ_i, B_i, a_i, b_i, c_i, $i = 1, 2$, denote constants which are determined from the physical properties of the system. Definitions of these constants, together with their numerical values for the hydrogen-oxygen reaction, are given in Appendix I. The quantities A_s, $s = 0, 1, 2, \ldots$ denote the coefficients in the expansion in a Legendre series of the perturbation potential assumed responsible

for chemical transition, namely,

$$\mathcal{H}(\vec{\xi}, \vec{\eta}) = \sum_{s=0}^{\infty} A_s \left(s+\tfrac{1}{2}\right) P_s\left(\frac{\vec{\xi}\cdot\vec{\eta}}{|\vec{\xi}|\cdot|\vec{\eta}|}\right),$$

where $\vec{\xi}$, $\vec{\eta}$ denote the vectors joining the atoms of the initial and final molecules, respectively. Numerical values of the A's are given in Appendix I.

In the cases of interest, it has been found that, to a good approximation, one may take $A_s = 0$ for $s > 3$. This assumption leads to considerable simplification in the calculations, for then the quantities C_{kl}^{KL} vanish unless $|k - L| \leq 3$, $|l - K| \leq 3$.

From the computational point of view, the two major difficulties are the calculation of the double integral C, and the evaluation of the appropriate Bessel functions. We shall consider these in turn.

Evaluation of the Double Integral

Various analytical methods were employed in an effort to reduce the double integral in G to a convenient computing form, but we were unable to obtain any suitable results. It seems unlikely that one could find a closed form for G, and the various efforts to expand in a series led to slowly converging terms of very great complexity. Accordingly, it has been decided to evaluate G directly by means of numerical quadrature.

It will be seen that this approach places the burden of the work on the calculation of large numbers of Bessel functions. Thus, it becomes important to use a quadrature formula which requires the fewest possible number of points. In view of the weight function $\exp\left[-\frac{1}{2}(\alpha^2+\beta^2)\right]$ which appears in the integrand, the appropriate integration formula to use here is the Gauss-type quadrature based upon the Hermite polynomials.(2)

The optimum number of points to be used in this quadrature has been estimated by examination of the errors obtained in the numerical integration. For integrands with parameters in the range of interest of the hydrogen-oxygen reactions, and for transitions up to the third excited vibrational level (m, n = 0, 1, 2, 3), we have found that the error resulting from a six-point quadrature formula in each variable is well less than half of one percent. A five-point formula was found to yield errors up to ten percent, particularly at the higher vibrational levels. Accordingly, the double integrals in G will be evaluated by means of the six-point formula, thus requiring that each integrand be evaluated at 36 points.

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(2) H. E. Salzer, R. Zucker, and R. Capuano, "Tables of the Zeros and Weight Factors of the First Twenty Hermite Polynomials", J. Research Nat. Bur. Stds., (48) 1952 pp. 111-116.

The final integration for the transition probability will be performed by means of a Gauss-type quadrature based upon the Laguerre polynomials[3]. After suitable rearrangement, the transition probability will then be calculated on SEAC in the following form:

$$P_{kl}^{nm} = \frac{Q}{T^{3/2}} \, e^{-\frac{1}{kT} \max(E_1, E_2)} \cdot$$

$$\cdot \sum_{i=1}^{M} q_i \, x_i \, y_i \sum_{k,l} C_{kl}^{KL} \left[G_{nm}^{kl} \right]^2 ,$$

where

$$G_{nm}^{kl} = \sum_{r,s=1}^{N} f_{n,r} \, g_{m,s} \, J_{\lambda_k}\left(x_i\left(1 + a_1 \alpha_r + b_1 \alpha_s\right)\right) J_{\mu_l}\left(y_i\left(1 + a_2 \alpha_r + b_2 \alpha_s\right)\right);$$

$$x_i = B_1 \sqrt{T} \sqrt{u_i + \max(0, \gamma)} \; ;$$

$$y_i = B_2 \sqrt{T} \sqrt{u_i - \min(0, \gamma)} \; ;$$

$$f_{n,r} = p_r \left(1 + \frac{\alpha_r}{\theta_1}\right) h_n(\alpha_r) \; ;$$

$$g_{m,s} = p_s \left(1 + \frac{\alpha_s}{\theta_2}\right) h_m(\alpha_s) \; ;$$

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(3) H. E. Salzer and R. Zucker, "Tables of the Zeros and Weight Factors of the First Fifteen Laguerre Polynomials", Bull. Amer. Math Soc., (55) 1949, pp.1004-1012.

u_i = abscissa for Laguerre quadrature;

q_i = weight for Laguerre quadrature;

α_i = abscissa for Hermite quadrature;

p_i = weight for Hermite quadrature.

The quantity Q is defined in Appendix I.

It will be observed that with this formulation, it is necessary to calculate each Bessel function for MN^2 values of its argument. If we assume, as above, that the constants G^{KL}_{kl} vanish unless $|k-L| \leq 3$, $|l-K| \leq 3$, then, in each case, seven values of k and of l must be considered. With this range of k and l, and with N = M = 6, a total of about 3,000 Bessel functions is required for each transition. This would be prohibitive without fairly simple approximations to the Bessel functions in the range of interest.

Evaluation of the Bessel Functions

For the hydrogen-oxygen reactions, the Bessel functions $J_p(x)$ occur with parameters roughly in the range

$$p \geq 12, \qquad 1/2 < \frac{x}{p} < 2.$$

Asymptotic formulas for Bessel functions of large order and argument are well-known(4), both for the case $x < p$ and $x > p$. The accuracy of the formulas decreases as $x \to p$, however, and rather

(4) G. N. Watson, "Bessel Functions", Cambridge, 1945, Chap. VIII.

than add higher order approximations we have found it expedient to develop new formulas for the region $x \approx p$. By comparing the errors in the various approximations, we have found that the standard asymptotic formulas could be used in the regions $x/p < 0.85$, $x/p > 1.15$, and the new formula in the region $0.85 < x/p < 1.15$, with a maximum error of about five percent. The largest errors occur in narrow bands about the values $x/p = 1 \pm 0.15$, and for only the smaller values of p ($p \approx 12$), with the errors decreasing sharply away from these points. It is felt that errors in the integrations resulting from these approximations should not exceed about two percent. The formulas used in the computation of the Bessel functions are given in Appendix II.

The properties of the quantity C_{kl}^{KL} assumed above enable us to make a substantial reduction in the number of Bessel functions that need be computed. The orders of the Bessel functions have the form $\sqrt{C + k(k+1)}$ where C is a large constant ($C > 150$, say) and since we must have $|k-L| \leq 3$, there is only a small percentage variation in the orders within a given transition. Indeed, as k ranges from L to L + 3, the order of the Bessel function will increase by less than ten percent. This suggests that for $|k-L| \leq 3$, $J_{\lambda k}(x)$ can be obtained by means of an appropriate expansion about $J_{\lambda L}(x)$. We have developed approximate formulas for calculating $J_{p(1+\epsilon)}(x)$ in terms of $J_p(x)$ which, in the range of interest are in error by

at most about five percent for $p \approx 12$ with the error decreasing sharply with increasing p. It is felt that this approximation should result in errors not exceeding about two percent except possibly for the lowest rotational states where the error might be as high as five percent. The approximations are given in Appendix II.

It will be observed that, with this simplification, only one-seventh of the Bessel functions need be computed directly from the asymptotic formulas given above. Since a large portion of the computing time is devoted to the calculation of Bessel functions, this results in a major reduction in machine time for the problem. Indeed, without some approximation of this sort, the computing time for the procedure outlined here would be prohibitive.

Remarks on Coding

The work of coding the present calculation for SEAC begins with the formulation presented here. The major difficulties encountered in the coding have been chiefly concerned with storage limitations of the machine. In order not to exceed the machine capacity, it has been necessary to devise several flexible calculating routines that could be used for more than one purpose. Thus, for example, a single routine has been set up for calculating $J_p(x)$ in both regions $x/p < 0.85$ and $x/p > 1.15$.

The development of these procedures has been carried on jointly by representatives of Hydrocarbon Research, Inc. and the Computation Laboratory. At the present time, all of the major planning problems have been resolved, and the remainder of the work at the Computation Laboratory will be concerned with putting the various segments into a contiguous unit and with final checking of the code on SEAC.

Appendix I - Physical Constants

The physical constants employed in the calculation of the transition probabilities are defined as follows:

$$B_1 = \frac{\sqrt{2\mu_1 k}}{\hbar}\left(\frac{m_1}{m_1+m_2}\rho_1 + \rho_2\right);$$

$$B_2 = \frac{\sqrt{2\mu_2 k}}{\hbar}\left(\rho_1 + \frac{m_3}{m_2+m_3}\rho_2\right);$$

$$a_1 = \frac{\dfrac{m_1\rho_1}{(m_1+m_2)\theta_1}}{\dfrac{m_1}{m_1+m_2}\rho_1 + \rho_2}; \quad a_2 = \frac{\dfrac{\rho_1}{\theta_1}}{\rho_1 + \dfrac{m_3}{m_2+m_3}\rho_2};$$

$$b_1 = \frac{\rho_2}{\rho_1}\frac{\theta_1}{\theta_2}\frac{m_1+m_2}{m_1}a_1; \quad b_2 = \frac{\rho_2}{\rho_1}\frac{\theta_1}{\theta_2}\frac{m_3}{m_2+m_3}a_2;$$

$$\theta_1 = \rho_1\sqrt{\frac{2\pi\nu_1}{\hbar}\frac{m_1 m_2}{m_1+m_2}}; \quad \theta_2 = \rho_2\sqrt{\frac{2\pi\nu_2}{\hbar}\frac{m_2 m_3}{m_2+m_3}};$$

$$\mu_1 = \frac{(m_1+m_2)m_3}{m_1+m_2+m_3}; \quad \mu_2 = \frac{m_1(m_2+m_3)}{m_1+m_2+m_3};$$

$$Q = \frac{t}{V}\frac{\sqrt{2\pi}\,\mu_2^{3/2}\rho_1^3\rho_2^3}{\hbar^2 I_1\theta_1\theta_2 B_1 B_2\sqrt{k}};$$

where

k = Boltzmann's constant.

ρ_1 = equilibrium distance between atoms of initial molecule

ρ_2 = equilibrium distance between atoms of final molecule.

ν_1 = fundamental vibration frequency of the initial molecule.

ν_2 = fundamental vibration frequency of the final molecule.

I_1 = moment of inertia of initial molecule.

m_1 = mass of final atom ,

m_3 = mass of initial atom ,

m_2 = mass of exchanging atom.

t = time

V = region of normalization of the wave functions.

The numerical values of the constants for the hydrogen-oxygen reactions are given below:

		$O_2 + H \rightarrow OH + O$	$H_2 + O \rightarrow OH + H$
B_1	$(°K)^{-1/2}$	.3173	.3660
B_2	$(°K)^{-1/2}$	.7406	.3291
a_1		.01633	.04593
a_2		.04066	.07448
b_1		.06201	.07278
b_2		.004574	.05551
θ_1		23.474	6.0155
θ_2		9.9434	9.9434
c_1		13.1	17.6
c_2		37.8	12.8

For the reaction $O_2 + H \rightarrow OH + O$,

$$\frac{E_1}{kT} = \frac{1000}{T}\left[2.228n + .002059\,K\,(K+1)\right],$$

$$\frac{E_2}{kT} = \frac{1000}{T}\left[5.252m + .02664\,L\,(L+1) + 9.1623\right].$$

For the reaction $H_2 + O \rightarrow OH + H$,

$$\frac{E_1}{kT} = \frac{1000}{T}\left[6.159n + .08497\,K\,(K+1)\right],$$

$$\frac{E_2}{kT} = \frac{1000}{T}\left[5.252m + .02664L\,(L+1) + 2.1295\right].$$

There is considerable uncertainty in the form to be employed for the chemical perturbation potential $\mathcal{H}(\vec{\xi}, \vec{\eta})$. We have found it convenient to fit this potential in the form

$$\mathcal{H}(\vec{\xi}, \vec{\eta}) = H_0 e^{-R(x+1)},$$

$$x = \frac{\vec{\xi} \cdot \vec{\eta}}{|\vec{\xi}| \cdot |\vec{\eta}|}, \qquad -1 \leq x \leq 1.$$

Here, $\vec{\xi}$ and $\vec{\eta}$ denote the vectors joining the atoms of the initial and final molecules, respectively. In this form, it will be noted that, for large R, the bulk of the contribution comes in the neighborhood of $x = -1$, corresponding to a linear configuration of the three atoms. The extent to which the contribution is limited to this region depends, of course, on the magnitude of R, and it would be valuable to explore the effect of changes in R upon the transition probabilities. Preliminary considerations in the case of the hydrogen-oxygen reactions suggest that we take $R = 5$, in which case the expansion of $\mathcal{H}$ in a Legendre series leads to the following values of the coefficients:

$$\frac{A_1}{A_0} = -.85, \quad \frac{A_2}{A_0} = +.52, \quad \frac{A_3}{A_0} = -.28.$$

If we take R = 10, we find

$$\frac{A_1}{A_o} = -.90, \quad \frac{A_2}{A_1} = +.73 \quad \frac{A_3}{A_o} = -.53$$

No attempt has been made, at this stage, to evaluate the constant H_o; its value will affect only the absolute reaction rate and not the relative values of the transition probabilities.

Appendix II - Formulas for Bessel Functions

The formulas for computing the Bessel functions are as follows: Let $z = 1 - y^2$, and let

$$A_p(z) = 1 + \frac{1}{p^2 z}\left\{.07031 - \frac{.4010}{z} + \frac{.3342}{z^2}\right\},$$

$$B_p(z) = \frac{3z - 5}{24\, p\, z\, |z|^{1/2}}.$$

For $y \leq .85$,

$$J_p(py) = \frac{e^{p\left[|z|^{1/2} - \arctan|z|^{1/2}\right]}}{2p\sqrt{y}\,|z|^{1/4}}\left[A_p(z) + B_p(z)\right].$$

For $y > 1.15$,

$$J_p(py) = \frac{1}{p\sqrt{y}\,|z|^{1/4}}\left[A_p(z)\cos\left\{p\left[|z|^{1/2} - \arctan|z|^{1/2}\right] - \frac{\pi}{4}\right\} + B_p(z)\sin\left\{p\left[|z|^{1/2} - \arctan|z|^{1/2}\right] - \frac{\pi}{4}\right\}\right].$$

For $.85 \leq y \leq 1.15$,

$$J_p(py) = \sqrt{\frac{\pi}{2y}}\cdot p^{-5/6}\left[.4473 - .0895(y-1) - .1491\,p^2(y-1)^3\right] + \sqrt{\frac{\pi}{2y}}\; p^{-7/6}\left[.4109\,p(y-1) - \frac{.0059}{p} - .2054\,p(y-1)^2 - .0685\,p^3(y-1)^4\right].$$

The formulas for calculating the effect of small changes in the orders of the Bessel functions are as follows:

For $y < .85$,

$$J_{p(1+\epsilon)}(py) = \left(1 - \frac{\epsilon}{2z}\right) e^{-p\epsilon\left[\operatorname{arctanh} |z|^{1/2} + \frac{\epsilon}{2|z|^{1/2}}\right]} J_p(py).$$

For $y > 1.15$,

$$J_{p(1+\epsilon)}(py) = \frac{\left(1 - \frac{\epsilon}{2z}\right)}{p\sqrt{y}\,|z|^{1/4}} \cdot$$

$$\cdot \left[A_p(z) \cos\left\{p\left[|z|^{1/2} - \arctan |z|^{1/2}\right] - \frac{\pi}{4} + \nu_\epsilon\right\}\right.$$

$$\left. + B_p(z)\left\{1 - \epsilon\,\frac{13z - 15}{z(3z-5)}\right\} \sin\left\{p\left[|z|^{1/2} - \arctan |z|^{1/2}\right] - \frac{\pi}{4} + \nu_\epsilon\right\}\right],$$

$$\nu_\epsilon = -p\epsilon\left[\arctan |z|^{1/2} - \frac{\epsilon}{2|z|^{1/2}}\right].$$